Fluid Mechanics and Its Applications

José María Montanero

Tip Streaming of Simple and Complex Fluids

Springer

Fluid Mechanics and Its Applications

Volume 137

The purpose of this series is to focus on subjects in which fluid mechanics plays a fundamental role. As well as the more traditional applications of aeronautics, hydraulics, heat and mass transfer etc., books will be published dealing with topics, which are currently in a state of rapid development, such as turbulence, suspensions and multiphase fluids, super and hypersonic flows and numerical modelling techniques. It is a widely held view that it is the interdisciplinary subjects that will receive intense scientific attention, bringing them to the forefront of technological advancement. Fluids have the ability to transport matter and its properties as well as transmit force, therefore fluid mechanics is a subject that is particulary open to cross fertilisation with other sciences and disciplines of engineering. The subject of fluid mechanics will be highly relevant in such domains as chemical, metallurgical, biological and ecological engineering. This series is particularly open to such new multidisciplinary domains. The median level of presentation is the first year graduate student. Some texts are monographs defining the current state of a field; others are accessible to final year undergraduates; but essentially the emphasis is on readability and clarity.

Springer and Professor Thess welcome book ideas from authors. Potential authors who wish to submit a book proposal should contact Dr. Mayra Castro, Senior Editor, Springer Heidelberg, e-mail: mayra.castro@springer.com

Indexed by SCOPUS, EBSCO Discovery Service, OCLC, ProQuest Summon, Google Scholar and SpringerLink

José María Montanero

Tip Streaming of Simple and Complex Fluids

Foreword by Alfonso M. Gañán Calvo

Springer

José María Montanero
University of Extremadura
Badajoz, Spain

ISSN 0926-5112 ISSN 2215-0056 (electronic)
Fluid Mechanics and Its Applications
ISBN 978-3-031-52767-8 ISBN 978-3-031-52768-5 (eBook)
https://doi.org/10.1007/978-3-031-52768-5

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Paper in this product is recyclable.

A mis padres, fuente de motivación y confianza a lo largo de mi vida

Foreword

This book reflects the outcome of more than 20 years of collaboration between the author and me, exemplified by our completion of numerous joint research projects back to 2002. The idea to create a book as a joint celebration of the 25th anniversary of the first publication on Flow Focusing (Gañán-Calvo 1998, Phys. Rev. Lett. 80, 285) was born in September 2022. However, it is one thing to suggest the joint draft of a book, and quite another to organize it, put the material in perspective, and write it. In this regard, José María Montanero has been exceptionally effective and focused, without concessions to superfluous considerations and ramifications. Thus, I firstly express my gratitude to José María for compiling the work on the development initiated by my invention of Flow Focusing in 1994, including its impact on the related field of fluid physics or other relevant domains, which was brought to fruition thanks to the collective endeavor of contemporary researchers, leading their own ideas and developments or being inspired by the concept.

Flow Focusing has revolutionized microfluidics since Howard Stone and colleagues envisioned a way to incorporate its basic geometry (Gañán-Calvo, US Pat 6,116,516) into PDMS in a two-dimensional or flat format. Their famous publication (Anna, Bontoux and Stone 2003, Appl. Phys. Lett. 82, 364) established this technique as a standard microfluidic method in the scientific literature, where one can find other configurations derived from Flow Focusing, such as that of Utada et al. 2005, Science 308, 537. This technique allows the continuous production of very uniform microbubbles, microdroplets or double or triple microemulsions with a geometric deviation close to one.

One of the strongest illustrations of the enabling capacity of Flow Focusing is its application in Serial Femtosecond Crystallography (SFX). Flow Focusing is capable of generating aerodynamically focused liquid microjets that exhibit extraordinary stability, travel at very high velocities, and possess perfectly controllable sizes as minute as a micron. Previously, these features could only be achieved with electrospray techniques (also described in this volume). The concept of sequentially exposing particles such as microcrystals to electromagnetic beams using Flow Focusing was patented in 2002 (Gañán-Calvo et al. 2003, Spanish patent file 200301500). In November 2007, I was invited by John Spence and Bruce Doak and

toured their laboratory at Arizona State University. The concept for SFX, which merges X-ray molecular imaging (Chapman et al. 2006, Nat. Phys. 2, 839) with Flow Focusing, originated from Henry Chapman, collaborating with Spence and others (Chapman et al. 2011, Nature 470, 73). Thanks to Flow Focusing, now small biological samples such as protein microcrystals can be sequentially probed by ultra-powerful and focused photon beams (X-ray Free Electron Lasers, XFELs) of femtosecond duration. The high repetition rates of the X-ray pulses at such facilities enable thousands of measurements per second to enable the rapid measurement of the 3D molecular structures in high-throughput experiments that follow complex biochemical reactions in time. Flow Focusing preserves the microcrystals in their necessary liquid environment and supplies fresh crystals to each X-ray pulse in a way that is gentle to these fragile samples. All this has established Flow Focusing as a standard sample handling procedure at XFEL facilities.

From a physics standpoint, Flow Focusing significantly advanced the development of capillary micro-focusing (tip streaming) techniques, going beyond proposing alternatives to the Taylor cone-jet electrospray method. In effect, mass production of particles with controlled sizes below 100 microns at a rate greater than 1 kHz per emission point could only be achieved through the application of intense electric fields to fluid interfaces, resulting in the appearance of cone-shaped points (reducible to singularities) on the charged surface, above a certain surface charge. Thanks to the discovery of Flow Focusing, it was evident that the concentration of forces leading to cusps and caustics—concepts thoroughly discussed by Jens Eggers (Eggers and Fontelos 2015, Singularities: formation, structure, and propagation. Cambridge UP)—could be utilized for the consistent generation of very small-sized streams. Mechanical means, such as a current forced through an orifice or an extensional current, thermal techniques like the surface tension gradient produced by thermal concentration, and even chemical gradient procedures, can all be considered. These techniques are apt to generate controlled points of force concentration (tips), which can lead to micro-emissions of fluid from localized areas (streaming) due to the localized concentration of stresses or mass forces against surface tension and viscosity.

The fundamental point of the book authored by my esteemed colleague becomes evident through the first two figures of the initial chapter, taken from one of our papers. When I received the National Research Award from the King of Spain in February 2010 for my invention of Flow Focusing, I explained its use in mass-producing controlled size and structured templates at the micro and nano-scale. This process is critical in several high-end industries, including pharmaceuticals, chemicals, food, and electronics. During the presentation, an audience member asserted that the use of mass-produced micro-templates was not a new concept, as it had been previously researched and implemented. I responded that whatever the age of the templating concept, Flow Focusing facilitates the mass production of particles in varying sizes and shapes, such as drops, bubbles, or microcapsules, with an extreme precision of control and statistical dispersion. No other mechanical method can produce them with such accuracy and high output volume. Now, tip streaming not only generalizes the concept introduced by Flow Focusing but also gathers a plethora of tiny, elusive, yet critical processes to controllably disaggregate immiscible fluids.

In summary, José María Montanero has placed in your hands, dear reader, an extraordinary and up-to-date compendium of all the current knowledge related to the controlled disintegration of one or more immiscible fluids into another (or vacuum), either stationary or non-stationary, by means of singular stress concentration. In this sense, a wide variety of processes leading to singular stress concentrations are considered, obviously beyond Flow Focusing, such as the implosion of surface cavities (bubble bursting). A very detailed discussion is also given on the stability of the generated flows in the case of the consideration of stationary emission flows.

In addition, the author provides a unique insight into the influence of the complex molecular structure and non-Newtonian nature of the fluids involved in the disintegration process. Such a compendium aims to serve as a primary reference for future researchers in the field. As Plutarch put it, "Knowledge is not a vessel to be filled, but a fire to be kindled."

Sevilla, Spain
November 2023

Alfonso M. Gañán-Calvo

Preface

Tip streaming is an elusive but fascinating phenomenon. Under particular conditions, some external actuation of hydrodynamic or electrohydrodynamic nature stretches a droplet or film, which emits either tiny drops or an extremely thin fluid thread from its tip. The complexity of some versions of this phenomenon is difficult to find in other fields of mesoscale physics, even when the system adopts a steady or quasi-steady regime. Despite numerous works on tip streaming, there are still open fundamental questions about this phenomenon with significant repercussions at the technological level.

This book comprehensively describes the tip streaming in simple fluids and those containing surfactants and polymeric molecules. It summarizes the theoretical models and approximations commonly adopted to analyze this phenomenon. It provides relevant experimental results and presents the scaling laws for rationalizing those results. The stability of the flows leading to tip streaming is investigated experimentally and theoretically. Attention is paid to the effects of surfactant monolayers and viscoelasticity, including solutocapillarity, interfacial elasticity, surface viscosity, and extensional thickening caused by the polymer coil-stretch transition. This book also offers an overall perspective of the numerous technological applications of the tip streaming phenomenon.

We describe the physical mechanisms responsible for the onset of tip streaming driven by hydrodynamic and electrohydrodynamic forces. This text reviews relevant theoretical and experimental results of the periodic microdripping and continuous microjetting modes of tip streaming produced with microfluidic configurations such as electrospray, Flow Focusing, coflowing, selective withdrawal, and confined selective withdrawal. Similarities and distinctions among these techniques are analyzed. The physical mechanisms responsible for the instability of the microjetting mode are studied in detail.

We discuss the applicability of the above-mentioned configurations for controlled soft matter shaping and fragmentation on the submillimeter scale in several technological fields. Remarkable examples are the production of microemulsions and microencapsulation of active agents for the food and pharmacy industries, the atomization of charged liquids for analytical chemistry, and the ejection of ultra-fast

and ultra-thin jets for crystallography. The book collects the scaling laws used to rationalize experimental data and predict the outcome of the above-mentioned microfluidic configurations.

This text combines state-of-the-art experimental results and linear stability analysis to identify the instability mechanisms limiting the applicability of the above-mentioned microfluidic configurations. In this way, the book connects experimental observations with fundamental aspects of tip streaming, bridging the microfluidic and fluid dynamicist communities. The connection between results obtained from the theoretical and empirical approaches will help experimentalists understand the fundamental aspects of their practical problems. This work may constitute a valuable guide for the large community working on hydrodynamic focusing and electrospray. It will help researchers in this fruitful area frame their results in a broad context.

Chapter 1 contextualizes the tip streaming phenomenon in the field of microfluidics. Also, we briefly describe the microfluidic configurations analyzed in this work and the ingredients adding complexity to the problem. Chapter 2 presents the equations governing the flows considered in the book in the presence of electric fields, surfactants, and viscoelasticity. Chapters 3 and 4 are methodological sections that discuss the theoretical and experimental approaches commonly used in the study of tip streaming. We devote Chaps. 5 and 6 to the analysis of the onset (transient) tip streaming caused by electrohydrodynamic and hydrodynamic means, respectively. This phenomenon substantially differs from the periodic and steady modes produced by microfluidic devices that allow the control of the dispersed phase flow rate. Chapter 7 describes in detail those devices and introduces the dimensionless numbers characterizing the flows. Chapters 8 and 9 review relevant works for the specific configurations. We start by discussing some fundamental results of electrospray. Chapter 9 analyzes the tip streaming produced by coflowing and hydrodynamic focusing. We reserve the last two chapters for gaseous Flow Focusing, which enjoys remarkable applications.

This publication contains many results and discussions resulting from the fruitful collaboration with my colleagues at the Universities of Extremadura and Seville over the last 20 years. I want to thank all of them for their essential contribution to this work. Without that contribution, it would have been impossible for me to write the present book. I want to thank Pr. Alfonso Gañán-Calvo for introducing me to this field and helping me with his novel ideas and inspiring suggestions. My very close and daily collaboration with Pr. Miguel A. Herrada has been indispensable for many of the studies presented in this book. Those studies are based on the numerical method he devised and perfected over the years. Also, I would like to acknowledge the helpful discussions with Pr. José M. López-Herrera. Worthy of special mention are my former Ph.D. students and now esteemed colleagues at the University of Extremadura; in alphabetical order, Alberto Ponce-Torres, Alejandro Rubio, Antonio Acero, Beatriz Muñoz, Conrado Ferrera, Emilio Vega, Guadalupe Cabezas, Manuel Rubio, and

Noelia Rebollo. They helped me with their generous effort and continuous support to conduct the work presented in this book.

Badajoz, Spain
November 2023

José María Montanero

Contents

Symbols

α	Womersley number in gaseous Flow Focusing
$\hat{\alpha}$	Fluid volume fraction
α^*, α	Dimensionless conductivity
β	Surfactant elasticity (strength)
Υ	Heat capacity ratio
Γ	Surfactant surface concentration (surface coverage)
Γ_∞	Maximum packing density
Γ_{eq}	Surfactant surface density at equilibrium
δ_g	Gaseous boundary layer thickness in Flow Focusing
δ_l	Liquid boundary layer thickness in Flow Focusing
δ_μ	Electrohydrodynamic Reynolds number
δF	Perturbation amplitude of the interface location
Δp_e	Effective pressure drop in electrospray
Δp	Applied pressure drop in Flow Focusing
Δp_l	Pressure drop in the liquid meniscus of Flow Focusing
$\varepsilon^{(j)}$	Electrical permittivity of the phase j
ε^*	Complex dielectric constant
ε', ε	Relative permittivity
ε''	Dielectric loss
ε_o	Outer dielectric medium permittivity
$\dot{\varepsilon}$	Strain rate
θ_a	Advancing contact angle
θ_r	Receding contact angle
θ_T	Taylor cone semiangle
$\kappa_T^{(j)}$	Thermal conductivity of the phase j
κ_{Ti}	Inner phase thermal conductivity
κ_{To}	Outer phase thermal conductivity
κ^s	Dilatational surface viscosity
κ	Twice the mean curvature of the interface
κ_1	Curvature along the meridian

κ_2	Curvature along the parallel
κ_{tip}	Tip curvature
$\lambda_{\mu}^{(j)}$	Dilatational coefficient of viscosity of the phase j
$\lambda_{\mu o}$	Dilatational coefficient of viscosity of the outer phase
λ_D	Debye layer thickness
$\lambda_s^{(j)}$	Stress relaxation time evaluated in the phase j
$\lambda_r^{(j)}$	Stress retardation time evaluated in the phase j
λ_e	Extensional relaxation time
$\hat{\lambda}_D$	Thickness of the surfactant boundary layer
$\hat{\lambda}$	Inner to outer viscosity ratio in a extensional flow
Λ	Diameter ratio
$\mu^{(j)}$	Viscosity of the phase j
$\mu_p^{(j)}$	Polymer viscosity of the phase j
$\mu_s^{(j)}$	Solvent viscosity of the phase j
μ^s	Shear surface viscosity
μ	Viscosity, ratio of the outer to the inner viscosity
$\hat{\mu}$	Ratio of the inner to the outer viscosity
μ_0	Viscoelastic solution viscosity
μ_i	Inner phase viscosity
μ_o	Outer phase viscosity
$\rho^{(j)}$	Density of the phase j
ρ_i	Inner phase density
ρ_o	Outer phase density
ρ	Density, ratio of the outer to the inner density
$\hat{\rho}$	Ratio of the inner to outer density
$\rho_e^{(j)}$	Net free charge density in the phase j
σ	Surface tension
σ_0	Surface tension of the clean interface
$\hat{\sigma}$	Surface tension relative to its characteristic value
σ_{eq}	Surface tension of a surfactant-covered interface at equilibrium
σ_e	Surface charge density
$\tau^{(j)}$	Deviatoric stress tensor in the phase j
$\tau_p^{(j)}$	Polymer contribution to the deviatoric stress in the phase j
$\tau_s^{(j)}$	Solvent contribution to the deviatoric stress in the phase j
$\tau_M^{(j)}$	Maxwell stress in the phase j
τ_{Ma}	Marangoni stress
τ_s	Viscous surface stress
τ_{sn}	Normal viscous surface stress
τ_{st}	Tangential viscous surface stress
$\phi^{(i)}$	Electric potential in the inner phase
$\phi^{(o)}$	Electric potential in the outer phase
χ	Electric Bond (Taylor) number
$\omega_{n,m}$	Complex eigenfrequency of the mode (n, m)
a	Mother drop radius

$\mathbf{A}^{(j)}$	Conformation tensor in the phase j
Ai	Airy function
B	Bond number
$B^s_{\boldsymbol{\mu}}$	Boussinesq number based on the shear surface viscosity
$B^s_{\boldsymbol{\kappa}}$	Boussinesq number based on the dilatational surface viscosity
Ca	Capillary number
Ca_G	Capillary number based on the extensional flow intensity
Ca_{tip}	Capillary number based on the tip velocity
Ca_o	Outer phase capillary number
Ca_i	Inner phase capillary number
$\overline{Ca}$	Capillary number based on the interface velocity
$c_v^{(j)}$	Specific heat coefficient of the phase j
$c^{(j)}$	Volumetric monomer concentration in the phase j
$c_s^{(j)}$	Surfactant concentration on the interface side j
c_∞	Reservoir surfactant concentration
c_{cmc}	Critical micelle concentration
d_o	Characteristic (intrinsic) diameter scale of electrospray
d_d	Droplet diameter
d_b	Bubble diameter
d_j	Jet diameter
d_j^{FF}	Jet diameter predicted by the Flow Focusing formula
$\mathbf{D}^{(j)}$	The deformation rate tensor evaluated in the phase j
$\mathscr{D}$	Diffusion coefficient
$\mathscr{D}_c^{(j)}$	Diffusion coefficient for the surfactant as monomers
$\mathscr{D}_m^{(j)}$	Diffusion coefficient for the surfactant as micelles
$\mathscr{D}_s$	Surfactant surface diffusion coefficient
$\mathscr{D}_k$	Diffusion coefficient of the k-species in electrospray
D_o	Focusing orifice diameter
$\mathscr{E}_j$	Dimensionless electric strength
E_o	Characteristic electric field in electrospray
F	Distance of the interface from the z axis
F_0	Distance of the interface from the z axis in the base flow
$\mathscr{F}$	Faraday constant
$F_{\boldsymbol{\sigma}}$	Characteristic capillary force in Flow Focusing
F_p	Characteristic pressure force in Flow Focusing
$\mathbf{g}$	Gravitational acceleration
G	Intensity of the uniaxial extensional flow
H	Capillary-to-electrode/focusing orifice distance
$\hat{H}$	Dimensionless capillary-to-focusing orifice distance
H_{opt}	Optimum capillary-to-focusing orifice distance
$\mathbf{I}$	Identity matrix
$\mathbf{I}_s$	Tensor that projects any vector onto the interface
I	Electric current
I_s	Electric current convected by the surface

I_{se}	Electrostatic value of I_s
I_b	Electric current due to conduction across the bulk
I_o	Characteristic (intrinsic) electric current in electrospray
$\mathbf{j}$	Charge flux
$\mathscr{J}_{cm}^{(j)}$	Net rate of formation/breakup of micelles per unit volume
$\mathscr{J}_{\Gamma c}^{(j)}$	Net flux of surfactant from the phase j
k_B	Boltzmann constant
$k_a^{(j)}$	Adsorption constant for the phase j
$k_d^{(j)}$	Desorption constants for the phase j
$\widetilde{k}_a$	Adsorption Biot number
$\widetilde{k}_d$	Desorption Biot number
$\widetilde{k}$	Complex wavenumber
$K^{(j)}$	Electrical conductivity of the phase j
l_b	Jet breakup length
L	Axial characteristic length in electrospray
L_j	Jet length
L^2	Finite extensibility parameter
La	Laplace number
$m^{(j)}$	Volumetric concentration of surfactant as micelles
m	Azimuthal number
Ma	Marangoni number
$\mathbf{n}$	Unit outward normal vector
$n_k^{(j)}$	Number of mols per unit volume of the k-species
Oh	Ohnesorge number
Oh_j	Jet Ohnesorge number
Oh_i	Inner phase Ohnesorge number
$\mathrm{Oh}_{\boldsymbol{\mu}}^s$	Ohnesorge number based on the shear surface viscosity
$\mathrm{Oh}_{\boldsymbol{\kappa}}^s$	Ohnesorge number based on the dilatational surface viscosity
$P^{(j)}$	Reduced pressure field in the phase j
Pe	Peclet number
Pe_s	Surface Peclet number
$\mathbf{q}^{(j)}$	Heat flux vector
q_R	Rayleigh limit of charge
q_o	Intrinsic charge scale of electrospray
Q	Flow rate, dimensionless flow rate in electrospray
Q_c	Characteristic (intrinsic) flow rate in electrospray
Q_i	Inner phase flow rate
Q_o	Outer phase flow rate
$Q_{i\min}$	Minimum inner phase flow rate
$Q_{\min}$	Minimum flow rate ratio
Q_r	Outer to inner phase flow rate ratio
Q_D	Flow Focusing characteristic flow rate
Q_v	Flow Focusing characteristic flow rate
$Q_{i\mathrm{opt}}$	Optimum flow rate in gaseous Flow Focusing

Q_d	Dragged liquid flow rate in gaseous Flow Focusing
$r_k^{(j)}$	Net production rate of the species k
$\hat{R}_g^{(j)}$	Gas constant of the phase j
R_g	Universal gas constant
R_j	Jet radius
R_i	Feeding capillary radius
R_d	Droplet radius
R_{FF}	Jet radius predicted by the Flow Focusing formula
R_μ	Viscous characteristic length of Flow Focusing
Re_i	Inner phase Reynolds number
Re_j	Jet Reynolds number
$\mathrm{Re}_{\mathrm{FF}}$	Reynolds number based on $\boldsymbol{R}_{\mathrm{FF}}$ and v_j^{FF}
s	Intrinsic (surface) coordinate
$t_{\rho\sigma}$	Inertio-capillary time based on the capillary radius
$\hat{t}_{\rho\sigma}$	Jet inertia-capillary time
$\tilde{t}_{\rho\sigma}$	Inertio-capillary time based on the droplet diameter
t_e	Electric relaxation time
t_o	Characteristic (intrinsic) time scale of electrospray
t_r	Residence time
$\mathbf{T}_s$	Viscous surface stress tensor
u	Radial component of the velocity field
$U_{\mu\sigma}$	Visco-capillary velocity
$U_{\rho\sigma}$	Inertio-capillary velocity based on the capillary radius
v_o	Characteristic (intrinsic) velocity scale of electrospray
v_j	Jet velocity
v_j^{FF}	Jet velocity predicted by the Flow Focusing formula
$\mathbf{v}_s$	Surface velocity
V_i	Inner phase velocity
w	Axial component of the velocity field
w_k	Ion mobility of the k-species
We_j	Jet Weber number
We_i	Inner phase Weber number
$\mathrm{We}_{\mathrm{FF}}$	Weber number based on $\boldsymbol{R}_{\mathrm{FF}}$ and v_j^{FF}
Wi	Weissenberg number
Wi_j	Jet Weissenberg number
z_k	Valence of the k-species
Z	Distance from the ejector orifice

Chapter 1
Introduction

Abstract This book's title requires clarifying two concepts: "tip streaming" and "complex fluid." In essence, tip streaming is the flow producing tiny drops or jets from the tip of a mother droplet, fluid meniscus, or liquid film. We devote the first part of this chapter to motivating and contextualizing the tip streaming phenomenon. We also introduce the microfluidic configurations commonly used to produce this singular flow. These configurations and their specific applications will be analyzed in more detail throughout the text.

The term "complex fluids" has been coined to refer to substances involving the coexistence of several phases, such as foams, suspensions, and emulsions. It also refers to fluids containing colloids and macromolecules, as well as liquid crystals and quantum fluids, among others. Here, we use this term to refer only to liquids containing surfactant molecules or polymer chains, which produce interfacial and bulk viscoelastic effects, respectively. As explained in other chapters, surfactants and polymers substantially alter the tip streaming flow in many technologically relevant applications. In the last part of this chapter, we briefly describe these two elements. We also introduce the effect of externally applied electric fields, which drive the flow in many tip streaming realizations.

Keywords Tip streaming · Complex fluids · Microfluidic configurations · Surfactant · Viscoelasticity

1.1 Matter Fragmentation, Shaping, and Deposition

Tip streaming can be regarded as a microfluidic technique to produce the fragmentation, shaping, and deposition of matter in its fluid phase on the submillimeter scale in a controlled manner. In this section, we briefly describe the advantages of tip streaming over traditional droplet-based microfluidics methods for those purposes. Specific applications of tip streaming will be discussed in other chapters.

J. M. Montanero, *Tip Streaming of Simple and Complex Fluids*, Fluid Mechanics and Its Applications 137, https://doi.org/10.1007/978-3-031-52768-5_1

1.1.1 Matter Fragmentation

The matter fragmentation produced by tip streaming on the submillimeter scale has applications in countless fields, such as industrial and chemical engineering, biotechnology, the food and agricultural industry, and advanced material processing. For instance, electrohydrodynamic tip streaming (electrospray) creates aerosols in mass spectrometry [1]. Pharmacy is a salient example of the tip streaming applicability [2]. In this field, functional products with complex morphologies must be manufactured in a controlled way. For the sake of illustration, we here consider this technological discipline to show the relevance of tip streaming in processing both simple and complex fluids.

Product manufacturing in pharmacy belongs to the technological field of chemistry. Reducing bulk reactants or ingredients to granular matter is a typical preparatory step in this field. Chemistry often makes use of top-down fluid-dynamical processes for this purpose. These processes involve forces and energies much smaller than those necessary to trigger chemical reactions, ensuring that the reactants' chemical nature is not altered [2].

The main features of the produced granular matter are the size, shape, and degree of homogeneity of the grains or particles. The particle size determines the surface-to-volume ratio of the processed bulk material, while the size homogeneity reflects how that ratio is distributed among the grains. Finally, the particle shape affects not only the chemical reaction rate of the product but also other mechanical processes undergone by the grains, such as self-assembly and patterning [3–6].

As mentioned above, fluid-dynamical processes are frequently applied to the bulk material to shape it into a desired morphology (i.e., a specific granular structure). These processes use the liquid phase as the starting state and the surface tension as the *mechanical mold*. If the characteristic lengths of the liquid internal structure are much smaller than the size of the produced fragments, then the shape resulting from the complete fragmentation is a sphere (drop). The spherical shape offers two fundamental advantages: it is reproducible and provides the minimum surface-to-volume ratio for a given volume [7, 8]. The cylindrical shape (the jet) is also reproducible, frequently appearing as an intermediate state during fragmentation. This shape is inherently ephemeral due to the capillary instability [9, 10] unless a sufficiently fast physicochemical process (drying, freezing, curing, …) causes a phase change of the liquid before the breakage.

Fluid-dynamical processes produce controlled or irregular fragmentation depending on the relative strength of the forces involved. If inertial forces are much larger than surface tension, fragmentation is turbulent and dominated by stochastic processes. On the contrary, processes driven by surface tension lead to laminar and smooth fragmentation (Fig. 1.1). As explained below, tip streaming techniques, such as flow focusing, can generate those capillary processes [2]. Figure 1.2 shows scanning electron microscopy photographs of Gem-loaded PLGA particles obtained by turbulent (Flow Blurring®) and laminar (Flow Focusing®) fragmentation followed by solvent extraction [11].

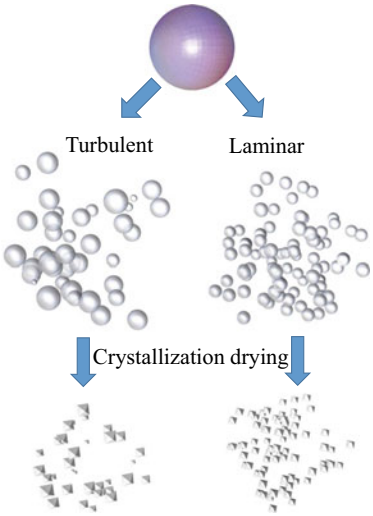

Fig. 1.1 Matter fragmentation: turbulent (flow blurring) versus laminar (flow focusing) fragmentation (reprinted from Ref. [2] with permission of Elsevier)

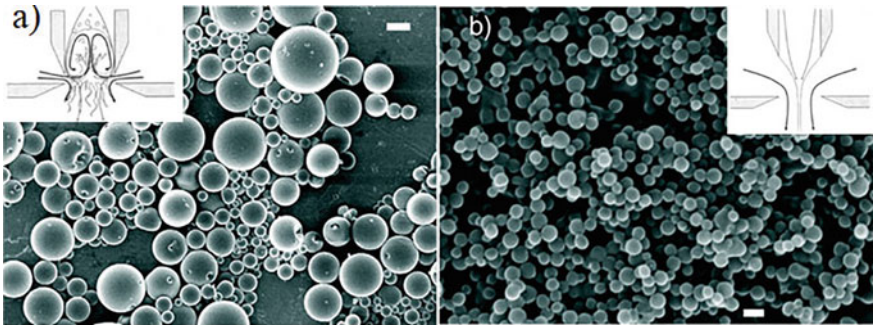

Fig. 1.2 Production of PLGA microparticles: flow blurring (**a**) versus flow focusing (**b**). Bars length: 1 μm (reprinted from Ref. [2] with permission of Elsevier)

1.1.2 Matter Shaping

Some tip streaming methods used for matter fragmentation can also be applied to shape a continuous phase on the submillimeter scale. This process has many applications in very diverse fields. For instance, flow focusing shapes a liquid volume into a fast micrometer jet, as discussed in Chaps 10 and 11. This technique has become the most common method for sample delivery in serial femtosecond crystallography [12].

One of the most remarkable examples of tip streaming for matter shaping is the formation of fibers. Fibers of micro and nanometer sizes possess many relevant

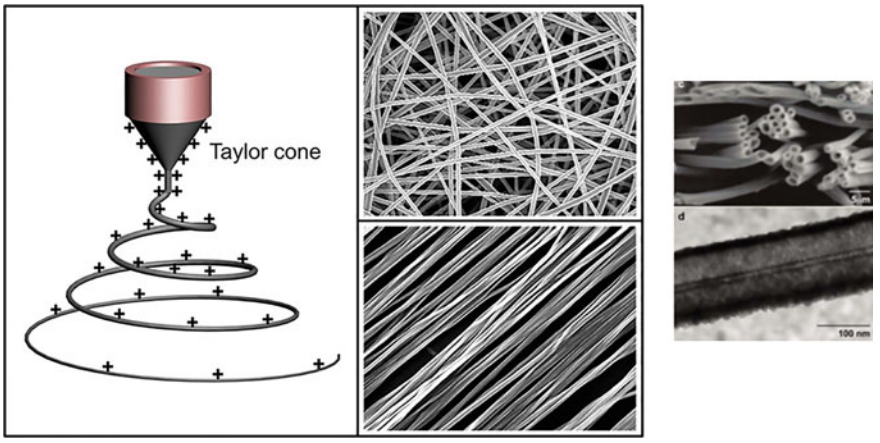

Fig. 1.3 (Left) Electrospinning (reprinted from Ref. [16] with permission of American Chemical Society). (Right) Hollow and coaxial fibers produced with electrospinning (reprinted from Ref. [17] with permission of American Chemical Society)

features, such as high and controllable surface area-to-volume ratios or excellent mechanical properties. Besides, the materials employed to form the fibers exhibit a great variety of physicochemical and biological properties. All these characteristics make micro and nanofibers and their mats particularly attractive for a vast class of applications, including filters, membranes, microelectronics, military, optics, or health and personal care, among many others [13]. Glass and silk fibers [14] have obvious applications in the telecommunications and textile industries, respectively.

Electrospinning has become one of the most popular methods to form micro and nanofibers. It allows the mass production of one-by-one continuous fibers with different morphologies from various polymers (Fig. 1.3). This tip streaming technique and its varied applications have been extensively reviewed over the last years (see, e.g., [13–15]). For this reason, the present work does not intend to describe this method in depth.

Fibers can also be produced from the viscoelastic counterparts of flow blurring [18] and flow focusing [19]. Analogously to what occurs in the Newtonian case, massive production of fibers with a high degree of polydispersity can be extruded with a turbulent gas flow. In contrast, quasi-monodisperse collections of fibers are obtained when the polymer solution is shaped in the laminar mode (Fig. 1.4).

1.1.3 Matter Deposition

Another scope of application of the tip streaming phenomenon is the deposition of a liquid phase on a substrate with submillimeter resolution in a controlled manner. A salient example of this is printed and flexible electronics. Polymers with high elec-

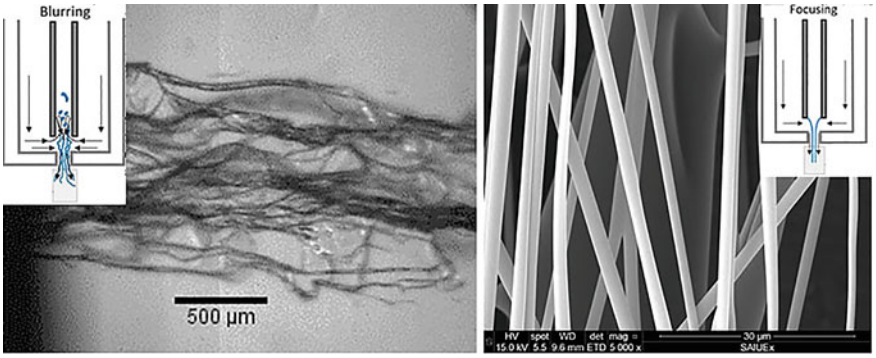

Fig. 1.4 Production of fibers from viscoelastic solutions: flow blurring (left) (reprinted with permission from Ref. [18]) versus flow focusing (right)

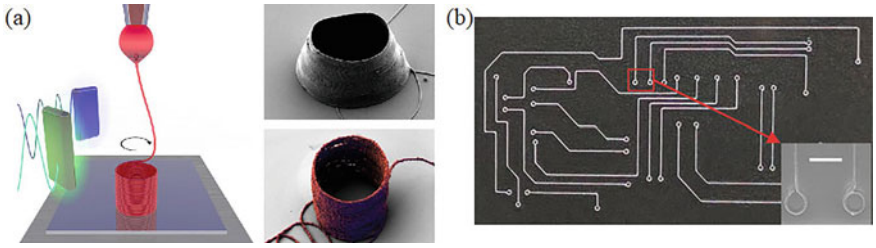

Fig. 1.5 **a** Ultrafast 3D printing of PEO cylindrical microstructures by controlling the voltage applied to two electrodes placed around the jet emitted in electrospinning [26] https://creativecommons.org/licenses/by/4.0/. **b** A circuit pattern fabricated by electrohydrodynamic printing on a glass slide (scale bar 500 µm) (reprinted with permission from Ref. [27])

trical conductivity, transparency, and physical and chemical stability are printed to form films. These films can be produced with inkjet printing [20], which constitutes a simple, flexible, and fast procedure to deposit/pattern a polymer with low cost, waste, and contamination. Inkjet printing has been used in the fabrication of organic solar cells [21, 22], electronic circuitry components [23], LEDs, sensors, and biosensors, among other electronic systems. Near-field electrospinning [24] and electrohydrodynamic printing [25] are tip streaming realizations used to emit and deposit polymeric jets much thinner than all the passages and orifices of the device (Fig. 1.5-left), increasing the spatial resolution of the printing technique (Fig. 1.5-right).

Bioengineering is another technological field that benefits from the smooth and gentle deposition of a liquid phase on a substrate. In extrusion bioplotting (also referred to as Direct Ink Write, DIW) [28–30], threads of "bioinks" are continuously extruded and deposited in spatially controlled filaments by a robotic system to build 3D structures. These bioinks usually consist of aqueous media, thermoreversible polymers, or polymer/hydrogel precursors combined with living cells. Tip streaming, as applied to bioplotting, allows reducing the diameter of the extruded threads and, therefore, of the deposited filaments.

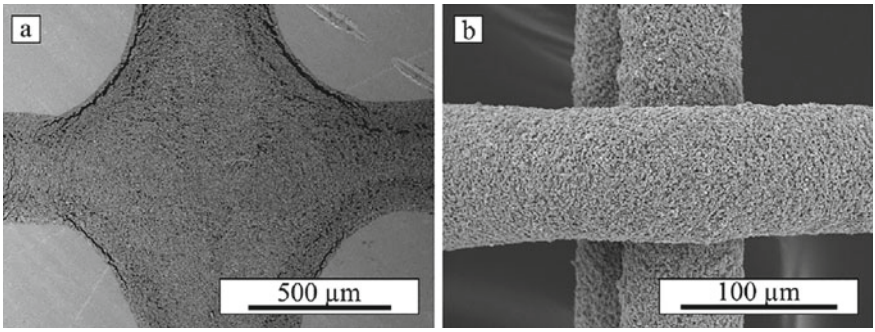

Fig. 1.6 SEM image of the intersection of ceramic (tricalcium phosphate, TCP) fibers produced with near-field electrospinning and deposited orthogonally in different layers under **a** low and **b** high UV exposure (reprinted from Ref. [31]).

Thin ceramic fibers are widely used in a range of applications ranging from catalysis to biomedical materials. Due to their high surface-to-volume ratio and superior strength, they are instrumental in fabricating composites with enhanced mechanical properties in terms of strength and fracture toughness. Direct ink writing is becoming an additive manufacturing technique of choice to fabricate scaffolds from bioactive materials like calcium phosphates or bioglasses. As occurs in bioplotting, one of the main limitations of this technique is that clogging of the extrusion nozzle prevents the production of ceramic struts less than 200 μm in diameter. Near-field electrospinning and other tip streaming methods can overcome this limitation (Fig. 1.6).

The applications described in this section are just some relevant examples of the utility of tip streaming. An exhaustive description of all these applications is beyond the scope of this text.

1.2 Droplet-Based Microfluidics

As mentioned above, numerous technological applications require the fragmentation of a continuous fluid phase into droplets/bubbles of different nature and morphology with narrow diameter distributions on the micro and nanometer scales. An ample variety of methods can be used for this purpose. Among them, we can distinguish drop-on-demand techniques from those in which droplets/bubbles are continuously generated [32, 33] (Fig. 1.7).

In a drop-on-demand technique, an external actuator produces the ejection of an individual droplet through the nozzle. Thermal and piezoelectric actuators are frequently used to this end. For instance, a resistor heats the ink until it vaporizes in the thermal inkjet method [34]. The quasi-instantaneous collapse of the resulting bubble drives the ejection of a droplet through the nozzle. In the piezoelectric inkjet method [33, 35], the droplet is ejected by the action of a pressure wave triggered

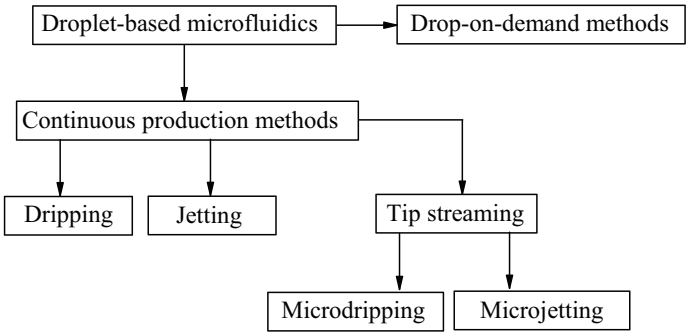

Fig. 1.7 Methods for producing droplets/bubbles on the micrometer and nanometer scales. Tip streaming is a route to microdripping and microjetting

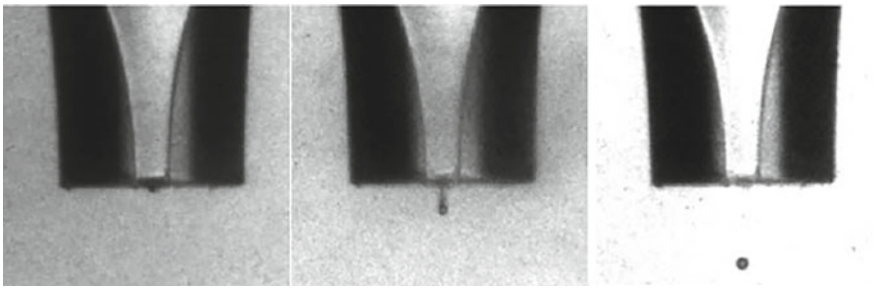

Fig. 1.8 Formation of a drop about 32 μm in diameter upon application of a voltage waveform to a piezoelectric transducer (reprinted from Ref. [36] with permission of AIP Publishing)

by the contraction of a piezoelectric element. Drop-on-demand techniques produce droplets with diameters similar to or even bigger than that of the ejecting nozzle. There are very few exceptions in which the diameter can be significantly reduced (Fig. 1.8) [36].

In a continuous production method, the nozzle ejects the fluid phase steadily. This ejection is powered by an external energy source constantly applied to that phase [37]. The nozzle can operate either in the dripping/bubbling or in the jetting mode depending on the ratio of the fluid kinetic energy to the interfacial one at the ejector orifice (Fig. 1.9). In the dripping/bubbling mode, drops/bubbles are emitted right behind the exit of the nozzle, while a fluid thread long compared with its diameter is formed in the jetting regime. In this case, the surface tension triggers the Plateau-Rayleigh instability [8, 9], which eventually leads to the breakup of the thread into a collection of droplets/bubbles whose diameters are commensurate with that of the jet (nozzle). The dripping/bubbling mode generally leads to very high monodispersity degrees, while the jetting regime yields larger production rates.

The distinction between the dripping/bubbling and jetting regimes is not always clear. In many applications, jetting becomes dripping/bubbling as the precursor fluid

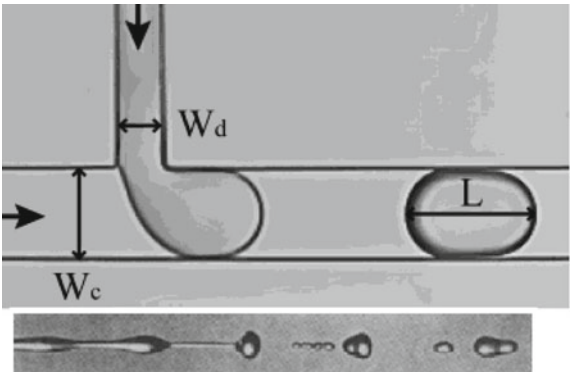

Fig. 1.9 Dripping in a T-junction (upper image) (reprinted from Ref. [38] under Creative Commons CC. BY. 4.0 license) and jetting (lower image) (reprinted from Ref. [39] with permission)

thread shortens. In this case, the free surface pinches off at the ends of the thread (the so-called end-pinching mechanism), also driven by surface tension [40, 41].

Reducing the droplet size and increasing the population's monodispersity degree is very important in many technological applications. However, these two features are somehow antagonistic because the size can be decreased only at the expense of monodispersity, and *vice versa*. Decreasing the size of the droplets requires overcoming the surface tension and viscosity force. This can only be achieved by injecting a significant amount of energy into the process, which generally increases the polydispersity in the usual atomization techniques. High monodispersity degrees can be obtained only if the energy is carefully focused on the droplet tip. When this occurs, the tip streaming phenomenon arises. As explained below, tip streaming is the route to the microdripping and microjetting modes, producing droplets with much smaller sizes than that of the microfluidic device (Fig. 1.7).

1.3 The Tip Streaming Phenomenon

Localized stresses can generate a point of force concentration (tip) that can lead to micro-emissions of fluid (streaming) from diminutive regions, overcoming the resistance of surface tension and viscosity. The stresses driving this tip streaming can have different origins (electrical, mechanical, chemical, thermal, …). This book will focus on the first two.

More than 100 years ago, Zeleny [42] and subsequently Wilson and Taylor [43] observed that when a pendant droplet or sessile bubble is subjected to a sufficiently strong electric field, a fine jet tapers from the tip of that droplet or bubble. Nolan [44] and Macky [45] observed a similar phenomenon with an electrically neutral levitating droplet. The conical shapes tapering the jets are called Taylor cones [46], and the jet emission is known as electrohydrodynamic tip streaming [47, 48]. More recently, numerous works have contributed to the understanding of the physical mechanism underlying the electrohydrodynamic tip streaming [48–51]. Fenn et al. [1] developed